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<b>(54) Title:</b> POLYMERIZATION CATALYST SYSTEMS, THEIR PRODUCTION AND USE  <b>(57) Abstract</b> <p>This invention is generally directed toward a supported catalyst system useful for polymerizing olefins. The method for supporting the catalyst system of the invention provides for a supported metallocene catalyst and alumoxane activator which when utilized in a polymerization process substantially reduces the reactor fouling and sheeting.</p>		

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**POLYMERIZATION CATALYST SYSTEMS, THEIR  
PRODUCTION AND USE**

5 This is a continuation-in-part of United States Patent Application Serial  
Number 08/265,532, filed June 24, 1994.

**FIELD OF THE INVENTION**

10 This invention relates to catalyst systems and to methods for their  
production and use in olefin polymerization. The invention particularly relates to a  
process for preparing a supported catalyst system for use in the gas phase, slurry  
phase or liquid/solution phase with improved reactor operability.

**BACKGROUND OF THE INVENTION**

15 It is desirable in many polymerization processes, particularly a slurry phase  
or gas phase process, to use a supported catalyst system. Generally these catalyst  
systems include a metallocene and alumoxane supported on a carrier, such as silica.  
For example, U.S. Patent No. 4,937,217 generally describes a mixture of  
trimethylaluminum and triethylaluminum added to an undehydrated silica to which  
a metallocene catalyst component is then added. EP-308177-B1 generally  
describes adding a wet monomer to a reactor containing a metallocene,  
20 trialkylaluminum and undehydrated silica. U.S. Patent Nos. 4,912,075, 4,935,397  
and 4,937,301 generally relate to adding trimethylaluminum to an undehydrated  
silica and then adding a metallocene to form a dry supported catalyst system. U.S.  
Patent No. 4,914,253 describes adding trimethylaluminum to undehydrated silica,  
adding a metallocene and then drying the resulting supported catalyst system with  
25 an amount of hydrogen to produce a polyethylene wax. U.S. Patent Nos.  
5,008,228, 5,086,025 and 5,147,949 generally describe forming a dry supported  
catalyst system by the addition of trimethylaluminum to a water impregnated silica  
to form alumoxane in situ and then adding the metallocene. U.S. Patent Nos.  
4,808,561, 4,897,455 and 4,701,432 describe techniques to form a supported  
30 catalyst system where the inert carrier, typically silica, is calcined and contacted  
with a metallocene(s) and an activator/cocatalyst component. U.S. Patent No.  
5,238,892 describes forming a dry supported catalyst system by mixing a  
metallocene with an alkyl aluminum and then adding undehydrated silica. U.S.  
Patent No. 5,240,894 generally pertains to forming a supported  
35 metallocene/alumoxane catalyst system by forming a metallocene/alumoxane

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reaction solution, adding a porous carrier, and evaporating the resulting slurry to remove residual solvent from the carrier.

While all these supported catalysts are useful, it would be desirable to have an improved metallocene catalyst system which in producing polymers does not  
5 foul the reactor. Particularly in a slurry or gas phase polymerization process, using these catalysts systems, there is a tendency for reactor operation problems during polymerization. During a typical gas phase polymerization process fines within the reactor often accumulate and cling or stick to the walls of a reactor. This phenomenon is often referred to as "sheeting". The accumulation of polymer  
10 particles on the reactor walls, the recycling lines and cooling system results in many problems including poor heat transfer during the polymerization process. Polymer particles that adhere to the walls of the reactor and can continue to polymerize and often fuse together and form chunks, which can be detrimental to a continuous polymerization process. Similarly, in a bulk liquid propylene  
15 polymerization process, using these catalyst systems there is a tendency for polymer particles to agglomerate and cling or stick to the walls of the reactor. This too can be detrimental to such a continuous process.

It would be highly desirable to have an improved polymerization catalyst system that in a polymerization process would significantly enhance reactor  
20 operability and provide an improved polymer product.

#### SUMMARY OF THE INVENTION

This invention is generally directed towards a new polymerization catalyst system, to methods for its manufacture and to its use in a polymerization process.

In one embodiment an improved method is provided to produce a  
25 supported bulky ligand transition metal catalyst system by contacting a porous support with a reaction product of a metallocene catalyst component and an alumoxane in a solution, the total volume of the reaction product being less than about four times the total pore volume of the porous support, preferably less than that amount at which a slurry is formed and wherein the metallocene catalyst  
30 component is a chiral, Group 4, 5 or 6 transition metal, bridged, substituted bisindenyl.

In yet another embodiment of the invention, there is provided a process for producing polypropylene polyolefins by contacting propylene monomer, optionally with a comonomer in the presence of the catalyst system described above.

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**DETAILED DESCRIPTION OF THE INVENTION****Introduction**

This invention is generally directed toward a supported catalyst system useful for polymerizing olefins. The method for forming the catalyst system of the invention involves supporting a metallocene catalyst component or compound with

5 an alumoxane activator or cocatalyst.

It has been discovered that catalyst systems prepared with a high molar ratio of the metal content of the alumoxane to the transition metal of the metallocene compound have high activity but also tend to foul during

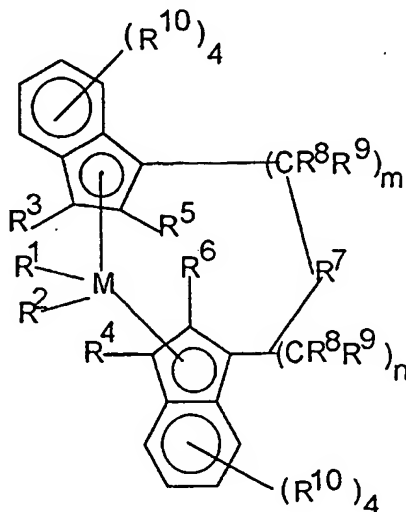
10 polymerization. By reducing the amount of alumoxane to transition metal, the fouling tendency is reduced but so is catalyst activity. It has been discovered that in forming the supported catalyst system of the invention, when the volume of the metallocene and the catalyst compound alumoxane solution is less than four times the pore volume of a porous support, preferably between less than the amount

15 required to form a slurry and above one times the pore volume of the porous support, catalyst activity is maintained and in many instances increased while fouling is reduced and in many instances eliminated. Making the catalyst system of the invention this way results in a simple, commercially useful and cost effective supported catalyst system. Also, the catalyst system of this invention results in a

20 high bulk density polymer product having improved particle morphology.

**Metallocene Catalyst Component of the Invention**

The metallocene components employed in the present invention comprise a Group 4, 5, or 6 transition metal, biscyclopentadienyl derivatives, preferably bis-indenyl metallocene components having the following general structure:



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wherein  $M^1$  is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium;

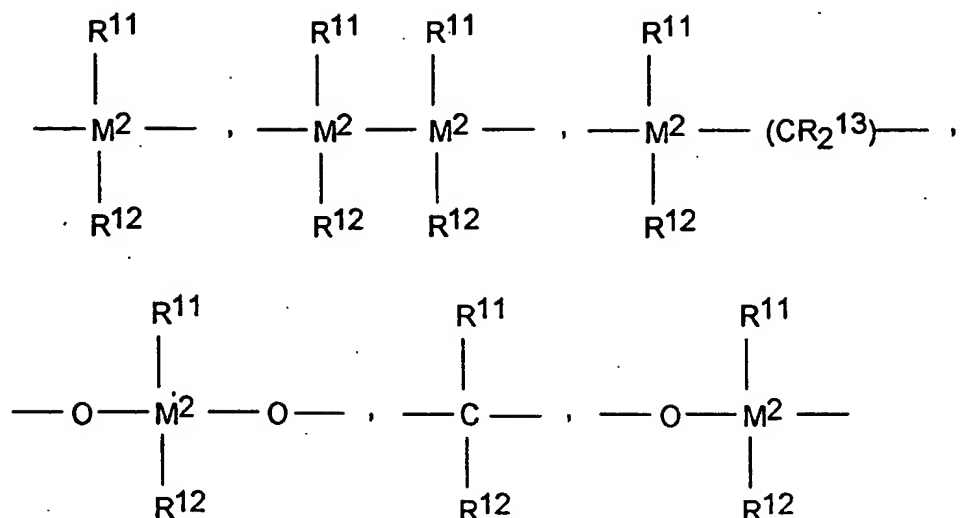
5            $R^1$  and  $R^2$  are identical or different, are one of a hydrogen atom, a  $C_1$ - $C_{10}$  alkyl group, preferably a  $C_1$ - $C_3$  alkyl group, a  $C_1$ - $C_{10}$  alkoxy group, preferably a  $C_1$ - $C_3$  alkoxy group, a  $C_6$ - $C_{10}$  aryl group, preferably a  $C_6$ - $C_8$  aryl group, a  $C_6$ - $C_{10}$  aryloxy group, preferably a  $C_6$ - $C_8$  aryloxy group, a  $C_2$ - $C_{10}$  alkenyl group, preferably a  $C_2$ - $C_4$  alkenyl group, a  $C_7$ - $C_{40}$  arylalkyl group, preferably a  $C_7$ - $C_{10}$  arylalkyl group, a  $C_7$ - $C_{40}$  alkylaryl group, preferably a  $C_7$ - $C_{12}$  alkylaryl group, a  $C_8$ - $C_{40}$  arylalkenyl group, preferably a  $C_8$ - $C_{12}$  arylalkenyl group, or a halogen atom, preferably chlorine;

$R^3$  and  $R^4$  are hydrogen atoms;

$R^5$  and  $R^6$  are identical or different, preferably identical, are one of a  
15   halogen atom, preferably a fluorine, chlorine or bromine atom, a  $C_1$ - $C_{10}$  alkyl group, preferably a  $C_1$ - $C_4$  alkyl group, which may be halogenated, a  $C_6$ - $C_{10}$  aryl group, which may be halogenated, preferably a  $C_6$ - $C_8$  aryl group, a  $C_2$ - $C_{10}$  alkenyl group, preferably a  $C_2$ - $C_4$  alkenyl group, a  $C_7$ - $C_{40}$  -arylalkyl group, preferably a  $C_7$ - $C_{10}$  arylalkyl group, a  $C_7$ - $C_{40}$  alkylaryl group, preferably a  $C_7$ -  
20    $C_{12}$  alkylaryl group, a  $C_8$ - $C_{40}$  arylalkenyl group, preferably a  $C_8$ - $C_{12}$  arylalkenyl group, a  $-NR_2^{15}$ ,  $-SR^{15}$ ,  $-OR^{15}$ ,  $-OSiR_3^{15}$  or  $-PR_2^{15}$  radical, wherein  $R^{15}$  is one of a halogen atom, preferably a chlorine atom, a  $C_1$ - $C_{10}$  alkyl group, preferably a  $C_1$ - $C_3$  alkyl group, or a  $C_6$ - $C_{10}$  aryl group, preferably a  $C_6$ - $C_9$  aryl group;

25            $R^7$  is

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=BR<sup>11</sup>, =AlR<sup>11</sup>, -Ge-, -Sn-, -O-, -S-, =SO, =SO<sub>2</sub>, =NR<sup>11</sup>, =CO, PR<sup>11</sup>, or =P(O)R<sup>11</sup>;

5 wherein:

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group, preferably a C<sub>1</sub>-C<sub>10</sub> alkyl group, a C<sub>1</sub>-C<sub>20</sub> fluoroalkyl group, preferably a C<sub>1</sub>-C<sub>10</sub> fluoroalkyl group, a C<sub>6</sub>-C<sub>30</sub> aryl group, preferably a C<sub>6</sub>-C<sub>20</sub> aryl group, a C<sub>6</sub>-C<sub>30</sub> fluoroaryl group, preferably a C<sub>6</sub>-C<sub>20</sub> fluoroaryl group, a C<sub>1</sub>-C<sub>20</sub> alkoxy group, preferably a C<sub>1</sub>-C<sub>10</sub> alkoxy group, a C<sub>2</sub>-C<sub>20</sub> alkenyl group, preferably a C<sub>2</sub>-C<sub>10</sub> alkenyl group, a C<sub>7</sub>-C<sub>40</sub> arylalkyl group, preferably a C<sub>7</sub>-C<sub>20</sub> arylalkyl group, a C<sub>8</sub>-C<sub>40</sub> arylalkenyl group, preferably a C<sub>8</sub>-C<sub>22</sub> arylalkenyl group, a C<sub>7</sub>-C<sub>40</sub> alkylaryl group, preferably a C<sub>7</sub>-C<sub>20</sub> alkylaryl group or R<sup>11</sup> and R<sup>12</sup>, or R<sup>11</sup> and R<sup>13</sup>, together with the atoms  
 15 binding them, can form ring systems;

M<sup>2</sup> is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

R<sup>8</sup> and R<sup>9</sup> are identical or different and have the meanings stated for R<sup>11</sup>;

m and n are identical or different and are zero, 1 or 2, preferably zero or 1,

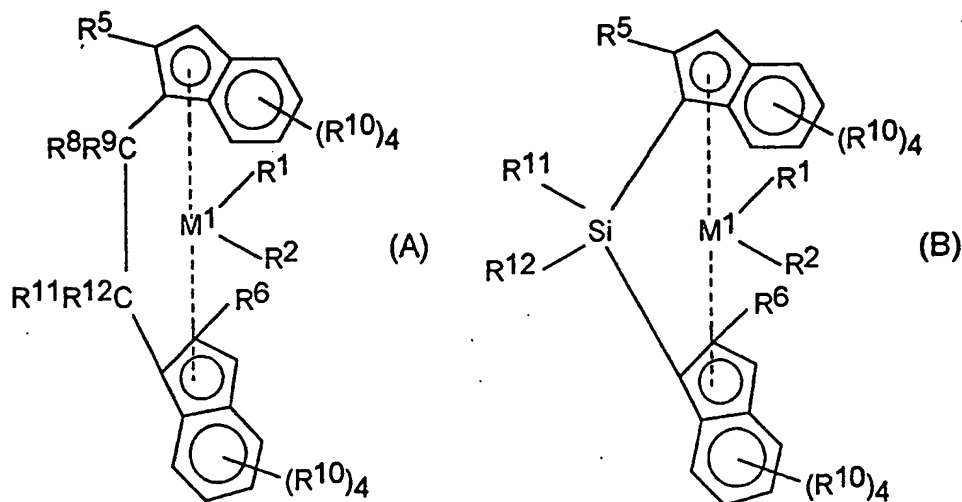
20 m plus n being zero, 1 or 2, preferably zero or 1; and

the radicals R<sup>10</sup> are identical or different and have the meanings stated for R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup>. Two adjacent R<sup>10</sup> radicals can be joined together to form a ring system, preferably a ring system containing from about 4-6 carbon atoms.

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Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

Particularly preferred metallocenes are compounds of the structures:



wherein:

$M^1$  is Zr or Hf,  $R^1$  and  $R^2$  are methyl or chlorine, and  $R^5$ ,  $R^6$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  have the above-mentioned meanings.

The chiral metallocenes are used as a racemate for the preparation of highly isotactic polypropylene copolymers.

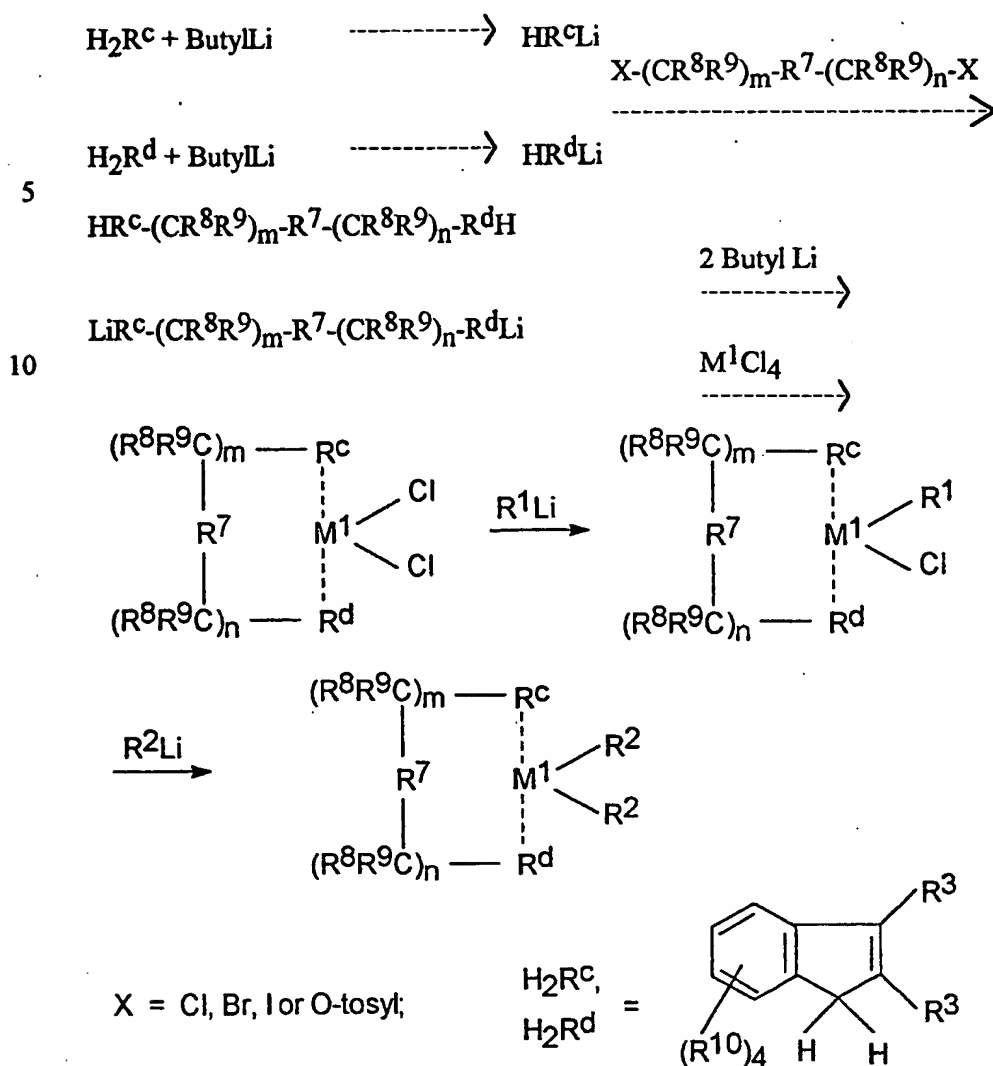
It is also possible to use the pure R or S form. An optically active polymer can be prepared with these pure stereoisomeric forms. It is preferred that the meso form of the metallocenes be removed to ensure the center (i.e., the metal atom) provides stereoregular polymerization.

Separation of the stereoisomers can be accomplished by known literature techniques. For special products it is also possible to use rac/meso mixtures.

Generally, the metallocenes are prepared by a multi-step process involving repeated deprotonations/metallations of the aromatic ligands and introduction of the bridge and the central atom by their halogen derivatives. The following reaction scheme illustrates this generic approach:



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The reader is referred to the Journal of Organometallic Chem., volume 288, (1958), pages 63-67, and EP-A- 320762, for preparation of the metallocenes described, both references are herein fully incorporated by reference.

**Illustrative but non-limiting examples of metallocenes include:**

**Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>**

**Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)ZrCl<sub>2</sub>;**

**Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)ZrCl<sub>2</sub>;**

20 Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>;

**Dimethylsilandiylbis (4-naphthyl-1-indenyl)ZrCl<sub>2</sub>,**

**Phenyl(Methyl)silandiylbis(2-methyl-4-phenyl-1-indenyl)ZrCl<sub>2</sub>,**

**Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl<sub>2</sub>,**

**Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl<sub>2</sub>,**

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- Dimethylsilandiylbis(indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
5 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl<sub>2</sub>,  
10 Phenyl(Methyl)silandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-ethyl-4-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2,4-dimethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl- $\alpha$ -acenaphth-1-indenyl)ZrCl<sub>2</sub>,  
15 Phenyl(Methyl)silandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl<sub>2</sub>,  
Phenyl(Methyl)silandiylbis(2-methyl-a-acenaphth-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
20 1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
25 Phenyl(Methyl)silandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Diphenylsilandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-ethyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl<sub>2</sub>,  
30 Phenyl(Methyl)silandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl<sub>2</sub>,  
Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl)ZrCl<sub>2</sub>, and the like.

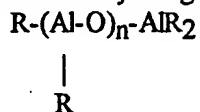
The metallocene catalyst components of this invention are described in detail in U.S. Patent Nos. 5,149,819, 5,243,001, 5,239,022, 5,296,434 and

- 35 5,276,208 all of which are herein fully incorporated by reference.

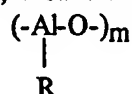
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**Activator Component of the Invention**

The activator or cocatalyst component of the present invention is alumoxane represented by the general formula:



5 for oligomeric, linear alumoxane and



for oligomeric, cyclic alumoxane, wherein n and m = 1-40, most preferably 3-20, and R is a C<sub>1-8</sub> alkyl group or R is an C<sub>6-18</sub> aryl group, or hydrogen, preferably a methyl group, or R can be mixtures of alkyl and aryl substituents.

10 There are a variety of methods for preparing alumoxane, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO 94/10180, all of which are  
15 fully incorporated herein by reference. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from a cloudy solution.

**Support Medium of the Invention**

For purposes of this patent specification the term "carrier" or "support" are  
20 interchangeable and can be any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides and resinous support materials such as polyolefin or polymeric compounds or any other organic support material and the like that has an average particle size greater than 10 µm.

25 The preferred support materials are inorganic oxide materials, which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal oxides. In a preferred embodiment, the catalyst support material include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-  
30 alumina are magnesia, titania, zirconia, and the like.

It is preferred that the carrier of the catalyst of this invention has a surface area in the range of from about 10 to about 700 m<sup>2</sup>/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from

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about 10 to about 500  $\mu\text{m}$ . More preferably, the surface area is in the range of from about 50 to about 500  $\text{m}^2/\text{g}$ , pore volume of from about 0.5 to about 3.5  $\text{cc/g}$  and average particle size of from about 20 to about 200  $\mu\text{m}$ . Most preferably the surface area range is from about 100 to about 400  $\text{m}^2/\text{g}$ , pore volume from about 0.8 to about 3.0  $\text{cc/g}$  and average particle size is from about 30 to about 100  $\mu\text{m}$ . The pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 $\text{\AA}$ , preferably 50 to about 500 $\text{\AA}$ , and most preferably 75 to about 350 $\text{\AA}$ .

#### Method of Producing the Catalyst System of the Invention

The supported catalyst system of the invention can be made in a variety of different ways.

For the purposes of this patent specification and appended claims the term "solution" includes a suspension, slurry or a mixture. Any compatible solvent capable of forming a solution or the like with at least one metallocene catalyst component and/or at least one alumoxane of the invention can be used. Non-limiting examples of solvents are those aliphatic, aromatic and saturated hydrocarbons, and cyclic hydrocarbons such as isopentane, heptane, toluene and the like. The more preferred solvents are the cyclic aliphatic and aromatic hydrocarbons, the most preferred of which is toluene.

The general support technique employed involves contacting, in a suitable solvent or other liquid, a metallocene catalyst component as described above with alumoxane or methylalumoxane (MAO) to form a soluble reaction product. The soluble reaction product is then contacted with a porous carrier, wherein the total volume of the soluble reaction product added to the carrier is less than four times the pore volume of the carrier, preferably less than the volume required to form a slurry. The resulting supported catalyst system can be dried to ensure that essentially all or most of the residual solvent is removed from the pores of the carrier. A free flowing supported catalyst system is obtained.

In one embodiment, a method to produce a free flowing, optionally prepolymerized supported catalyst system is provided, the method comprising the steps of: a) forming in a suitable solvent, a metallocene/alumoxane mixture wherein the metallocene is as described above; b) contacting the mixture of (a) with a porous carrier; wherein the total volume of the mixture added to the porous carrier is in the range of from less than that volume required to form a slurry to above one times the total pore volume of the porous support; c) removing essentially all the solvent; d) obtaining a supported catalyst system; and e)

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optionally prepolymerizing said supported catalyst system with one or more olefinic monomer(s), to form a prepolymerized supported catalyst system for the production of polymers of propylene or copolymers thereof, having a molecular weight of about 50,000 or greater, preferably 100,000 or greater, a melting point of about 135°C or greater, preferably about 140°C or greater, and more preferably about 145°C or greater and a bulk density of about 0.30 g/cm<sup>3</sup> or greater. The resulting granular polymer also has an average particle size of about 500 to about 1000 microns or greater. In the most preferred embodiment, the metallocene and the alumoxane components are combined to form a solution which is then added to a porous support.

In another embodiment, the dried supported catalyst system is washed or otherwise treated to remove weakly associated catalyst component(s). Any hydrocarbon may be used to wash the catalyst system, however, the hydrocarbon should be capable of dissolving the catalyst component and should be easy to dry from the support. Toluene and hexane are preferred.

Furthermore, in one embodiment of the invention the total volume of the metallocene/alumoxane solution is less than four times the pore volume of the porous support, more preferably less than three times, even more preferably less than two times, and most preferably less than one time the total pore volume of the porous support.

It is preferable to apply the solution containing catalyst component(s) to the support such that a homogeneous catalyst system is obtained, i.e., wherein the component(s) are evenly distributed on and within the support material particles. In a preferred embodiment, the total volume of solution containing metallocene and activator added to the support is in the range of from less than that volume at which a slurry is formed to above that volume equal to the total pore volume of the support, preferably from 2.5 times the total pore volume of the support to about 1.05 times the total pore volume of the support, more preferably from about 2.4 to about 1.1 times the total pore volume of the support, even more preferably from about 2.3 to about 1.2 times the total pore volume of the support, even more preferably from about 2.2 to about 1.25 times the total pore volume of the support, even more preferably from about 2.1 to about 1.27 times the total pore volume of the support, even more preferably from about 2.0 to about 1.3 times the total pore volume of the support, and even more preferably from about 2.0 to about 1.5 times the total pore volume of the support. Preferably, the solution is applied either

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dropwise or as a spray while the support is agitated or otherwise thoroughly mixed.

Generally, a slurry is formed when two phases are observable one of which contains all or most of the support material. The volume of solution required to reach this stage will vary depending upon among other things the type of support material and type of catalyst system components. Just prior to the point at which a slurry is formed, is a stage which is defined herein as the "mud" stage. At the mud stage, the solution volume is such that, while two phases are not visible, the support material is saturated and the support particles are firmly packed together. Prior to the mud stage, the volume of solution is such that the support material appearance ranges from dry and free flowing (even though the support may contain close to one pore volume of solution) to dry but slightly sticky to variously damp and clumpy such as is the appearance of variously wet sand.

In one embodiment, the volume of solution applied to the support material ranges from above one pore volume to that required to form a slurry, preferably from above one pore volume to that required to reach the mud stage. It should be recognized that catalyst systems formed in the mud stage are more difficult to mix and require longer drying times as compared to those prepared with less solution. Below one pore volume it may be difficult to obtain homogeneous coverage of the support material with the catalyst system components. This may lead to fouling.

It is contemplated by the invention that when preparing the catalyst system, the total amount of the is added to the porous support at one time, or, individually portions of the solution is added to the porous support such that at any point in time during the formation of the catalyst system the volume of solution is as described above.

The catalyst system of the invention can be dried and still contain an amount of solvent, for example, toluene, in its dried state, however, it is preferred that substantially all the solvent is removed. For the purposes of this patent specification and appended claims the term "substantially all of the solvent is removed" means that greater than about 90% of all the solvent is removed from the supported catalyst system when drying.

In another aspect of the invention, the ratio of the total volume of the metallocene catalyst component, alumoxane, and solvent to the total pore volume of the porous support material is in the range of 5:1 to 0.5:1, preferably 2.5:1 to 0.8:1, even more preferably 2:1 to 0.8:1, and most preferably 1:1 to 0.85:1.

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The procedure for measuring the total pore volume of a porous support is well known in the art. Details of one of these procedures is discussed in Volume 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, Analytical Chemistry 332-334 (March, 1956).

In another embodiment of the invention, the mole ratio of the metal of the alumoxane component to the transition metal of the metallocene component is in the range of ratios between 10:1 to 800:1, preferably 20:1 to less than 500:1, and most preferably 50:1 to less than 400:1.

The supported catalyst system of the invention may include a surface modifier such as that described in U.S. Patent Application No. 08/322,675 (fully incorporated herein by reference) and/or an antistatic agent, for example, those described in U.S. Patent No. 5,283,278, fully incorporated herein by reference. Non-limiting examples of antistatic agents include, alcohol, thiol, silanol, diol, ester, ketone, aldehyde, acid, amine, and ether compounds. Tertiary amine compounds are preferred. The antistatic agent can be added at any stage in the formation of the supported catalyst system of the invention, however, it is preferred that it is added after the supported catalyst system of the invention is formed, in either a slurry or dried state. In another embodiment of the invention, the supported catalyst system of the invention includes a polyolefin wax or tackifier or the like.

#### Polymerization Process of the Invention

The catalyst system of this invention is suited for the polymerization of monomers and optionally comonomers in any polymerization or prepolymerization process, gas, slurry or solution phase; even a high pressure autoclave process can be utilized. In the preferred embodiment a gas phase or slurry phase process is utilized, most preferably a bulk liquid propylene polymerization process is used.

In the preferred embodiment, this invention is directed toward the bulk liquid propylene slurry or gas phase polymerization or copolymerization reactions involving the polymerization of propylene with one or more of the alpha-olefin monomers having from 4 to 20 carbon atoms, preferably 4-12 carbon atoms, for example alpha-olefin comonomers of ethylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1, and cyclic olefins such as styrene. Other monomers can include polar vinyl, diolefins such as dienes, norbornene,

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acetylene and aldehyde monomers. The invention is particularly well suited to the polymerization reactions involving the polymerization of propylene. All the processes of the invention can be prepolymerized or polymerized or used in conjunction with an additive or scavenger component to enhance catalytic activity.

- 5        Optionally, the supported catalyst system of the invention can be prepolymerized. Prepolymerization has been found to improve particle morphology.

### EXAMPLES

- 10        In order to provide a better understanding of the present invention including representative advantages and limitations thereof, the following examples are offered.

- 15        In all examples the supernatant of a 30 wt% methyl alumoxane in toluene available from Albemarle Corporation, Baton Rouge, Louisiana was used. It is well known to those skilled in the art that methylalumoxane is a colloidal suspension in toluene ranging in consistency from a clear, gel free to an opaque gelled liquid, however, for the purposes of this invention gel free methylalumoxane is preferred.

#### 20        Example 1 Catalyst 1

- 25        A precursor solution was prepared by combining 11.858 g of 30 wt% gel free methylaluminoxane in toluene (61.05 millimoles Al) and 0.0747 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.156 millimoles Zr) with stirring. The precursor solution was added to 8.433 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.95. The finely divided, free-flowing solid was dried at reduced pressure (28+ in. Hg vacuum) and 40°C for 16 hours.
- 30        11.147 g catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 15.30 wt% Al.

#### Example 2 Catalyst 2

- 35        A precursor solution was prepared by combining 4.060 g of gel free 30 wt% methylaluminoxane in toluene (20.90 millimoles Al) and 0.0252 g of



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dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.053 millimoles Zr) with stirring. 2.318 g of toluene was added to dilute the precursor solution. 2.868 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub> was charged to a small beaker and the precursor was added all at once.

- 5 The ratio of liquid volume to total silica pore volume was 1.53. A spatula was used to stir the mixture which had the appearance of wet sand. The mixture was then dried at reduced pressure (28+ in. Hg vacuum) and 40°C for 16 hours. 3.908 g of free flowing catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 14.34 wt% Al.

10

### Example 3

#### Catalyst 3

- A precursor solution was prepared by combining 4.268 g of gel free 30 wt% methylaluminoxane in toluene (21.97 millimoles Al) and 0.0374 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.078 millimoles Zr) with stirring. The precursor solution was added to 4.250 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.68. The finely divided, free-flowing solid was dried at reduced pressure (28+ in. Hg vacuum) and 40°C for 16 hours. 5.209 g catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 10.68 wt% Al.

20

### Example 4

#### Catalyst 4

- 25 A precursor solution was prepared by combining 4.205 g of gel free 30 wt% methylaluminoxane in toluene (21.65 millimoles Al) and 0.0367 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.077 millimoles Zr) with stirring. The precursor solution was diluted with 1.648 g of toluene. The precursor was added to 4.125 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.97. The finely divided, free-flowing solid was dried at reduced pressure (28+ in. Hg vacuum) and 40°C for 16 hours. 5.032 g catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 10.96 wt% Al.

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**Example 5****Catalyst 5**

A precursor solution was prepared by combining 3.106 g of gel free 30 wt% methylaluminoxane in toluene (15.99 millimoles Al) and 0.0401 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.084 millimoles Zr) with stirring. 2.516 g of toluene was added to dilute the precursor. The precursor solution was added to 4.024 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.97. Drying of the finely divided, free-flowing solid was started at 25 in Hg vacuum and 35°C. Vacuum and temperature were increased to 29+ in. Hg vacuum and 60°C over 2.5 hours. Elemental analysis showed 0.13 wt% Zr and 7.93 wt% Al. Drying continued for an additional 1.0 hour. 4.862 g of free flowing catalyst was obtained.

**Example 6****Catalyst 6**

A precursor solution was prepared by combining 1.560 g of gel free 30 wt% methylaluminoxane in toluene (8.03 millimoles Al) and 0.0201 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.042 millimoles Zr) with stirring. 5.504 g of toluene was added to dilute the precursor solution. 2.005 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub> was charged to a small beaker and the precursor was added all at once. The ratio of liquid volume to total silica pore volume was 2.48. A spatula was used to stir the mixture which had the appearance of very wet sand or mud. The mixture was then dried at 25 in. Hg vacuum and 50°C until all liquid was removed then vacuum and temperature were increased to 29+ in. Hg vacuum and 60°C over 0.75 hours. Elemental analysis showed 0.15 wt% Zr and 8.63 wt% Al. Drying continued for an additional 1.0 hour. 2.444 g of free flowing catalyst was obtained.

30

**Example 7****Catalyst 7**

A precursor solution was prepared by combining 1.563 g of gel free 30 wt% methylaluminoxane in toluene (8.05 millimoles Al) and 0.0209 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.044 millimoles Zr) with stirring. 17.402 g of fresh toluene was added to dilute the precursor solution.

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2.011 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub> was charged to a small beaker and the precursor solution was added all at once. The ratio of liquid volume to total silica pore volume was 6.70. A spatula was used to stir the mixture and the slurry was dried at 25 in Hg vacuum and 25°C until all liquid was removed then vacuum and temperature were increased to 28+ in. Hg vacuum and 60°C over 1.25 hours. Drying continued for an additional 1.0 hour at 28+ in. Hg and 60°C for 1.0 hour. 2.395 g of free flowing catalyst was obtained.

10    Comparative Example 8  
      Catalyst 8

      A precursor solution was prepared by combining 6.932 g of gel free 30 wt% methylaluminoxane in toluene (35.68 millimoles Al) and 0.0227 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.048 millimoles Zr) with stirring. 12.384 g of toluene was added to dilute the precursor solution. 2.007 g of silica (MS948, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub> was slowly added to the precursor solution. The ratio of liquid volume to total silica pore volume was 6.70. The slurry was dried at 25 in Hg vacuum and 50°C until all liquid was removed then vacuum and temperature were increased to 28+ in. Hg vacuum and 60°C over 1.5 hours. Drying continued for an additional 1.0 hour at 28+ in. Hg and 60°C for 1.0 hour. 4.100 g of free flowing catalyst was obtained. Elemental analysis showed 0.091 wt% Zr and 20.48 wt% Al.

25    Example 9  
      Catalyst 9

      A precursor solution was prepared by combining 5.809 g of 30 wt% methylaluminoxane in toluene (29.91 millimoles Al) and 0.0365 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.076 millimoles Zr) with stirring. The precursor solution was added to 4.225 g of silica (MS948FF, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 200°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.93. The finely divided, free-flowing solid was dried under vacuum at 28+ in. Hg and at 40°C for 16 hours. 4.909 g catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 15.98 wt% Al.

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**Example 10****Catalyst 10**

A precursor solution was prepared by combining 5.692 g of 30 wt% methylaluminoxane in toluene (29.31 millimoles Al) and 0.0358 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.075 millimoles Zr) with stirring. Using the apparatus of Method 3, the precursor was added to 4.140 g of silica (MS948FF, 1.6 cc/g P.V., Davison Chemical Co.) previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.93. The finely divided, free-flowing solid was dried under vacuum at 22 in. Hg and 30°C for 1.5 hours then at 28+ in. Hg and 60°C for 2 hours. 5.344 g catalyst was obtained. Elemental analysis showed 0.10 wt% Zr and 15.58 wt% Al.

Examples 9 and 10 are illustrative of the catalyst of the invention and show that the silica dehydration temperature is not critical.

**Example 11****Catalyst 11**

A precursor solution was prepared by combining 4.339 g of 30 wt% methylaluminoxane in toluene (22.34 millimoles Al) and 0.0273 g of dimethylsilylbis(2-methylindenyl)zirconium dichloride (0.057 millimoles Zr) with stirring. The precursor solution was added to 3.079 g of silica (MS3040, 3.0 cc/g P.V., Philadelphia Quartz) previously heated to 700°C in air then 50°C in vacuo with N<sub>2</sub> purge. The ratio of liquid volume to total silica pore volume was 0.51. The finely divided, free-flowing solid was dried at reduced pressure under vacuum at 28+ in. Hg and at 40°C for 16 hours. 4.054 g catalyst was obtained. Elemental analysis showed 0.10 wt% Zr and 13.92 wt% Al. This example illustrates formation of the catalyst system of the invention with a different porosity carrier.

**POLYMERIZATION TESTS FOR CATALYSTS 1-11**

A sample of each of the supported catalyst made in the above Examples 1-11 was slurried in 2 ml of hexane and flushed with 250 mls of propylene into a 2 liter autoclave reactor, previously flushed with nitrogen, and containing triethylaluminum (0.5 ml of a 1 M solution in hexane) and 1000 ml of propylene, then the reactor is heated to a temperature of 65°C. The reaction was run for 1 hour, at which time, the reactor was cooled, vented, and purged with nitrogen for 20 minutes. After the nitrogen purge, the reactor was opened, and the product was collected and dried in vacuo for a minimum of 2 hours at 75°C. If there was

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any residual product (fouling) on the agitator or thermocouple, it was collected and weighed separately.

**TABLE 1**

5

Catalyst	Metals* Loading		Mole Ratio Al/Zr	Percentage Pore Volume	g Polymer/ g Catalyst	g Polymer/ mg Zr	Percent Fouling **
	Al	Zr					
1	7.24	0.019	381	95	2420	2017	~0.5
2	7.29	0.018	405	153	2767	2306	~0.5
3	5.17	0.018	287	68	2710	2258	~0.2
4	5.25	0.019	276	97	2865	2388	0.2
5	3.97	0.021	189	97	2642	—	0
6	4.00	0.021	190	250	2554	—	0
7	4.02	0.021	191	670	1876	—	0
C-8	17.78	0.024	740	670	2320	2549	11.8
9	7.08	0.021	337	93	2417	2014	<0.1
10	7.08	0.018	393	93	2292	2292	0
11	7.26	0.019	382	51	2182	2182	<0.1

\* millimoles per gram silica

\*\* grams fouled polymer per total polymer obtained times 100%

**Example 12**10 **Catalyst 12**

A precursor solution was prepared by combining 3.5022 g of 30 wt% gel free methylaluminoxane in toluene (18.03 millimoles Al) and 0.0654 g of dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.104 millimoles Zr) with stirring. Then 1.9488 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.95. The finely divided, free-flowing solid was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.5 hours. 5.12 g catalyst was obtained. Elemental analysis showed 0.07 wt% Zr and 8.98 wt% Al.

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**Example 13****Catalyst 13**

5 A precursor solution was prepared by combining 3.4997 g of 30 wt% gel free methylaluminoxane in toluene (18.02 millimoles Al) and 0.0648 g of dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.103 millimoles Zr) with stirring. Then 3.6798 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.)  
10 previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 1.25. The solid had the consistency of damp sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.5 hours. 4.99 g finely divided, free-flowing solid catalyst was obtained. Elemental analysis showed 0.07 wt% Zr and 8.64 wt% Al.

15

**Example 14****Catalyst 14**

A precursor solution was prepared by combining 3.5017 g of 30 wt% gel free methylaluminoxane in toluene (18.03 millimoles Al) and 0.0653 g of  
20 dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.104 millimoles Zr) with stirring. Then 9.3018 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica  
25 pore volume was 2.25. The solid had the consistency of wet sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.5 hours. 5.11 g catalyst finely divided, free-flowing solid was obtained. Elemental analysis showed 0.10 wt% Zr and 9.21 wt% Al.

**Example 15****Catalyst 15**

A precursor solution was prepared by combining 5.0489 g of 30 wt% gel free methylaluminoxane in toluene (25.992 millimoles Al) and 0.0649 g of  
35 dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.103 millimoles Zr) with stirring. Then 0.5014 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace,

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Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.95. The finely divided, free-flowing solid was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.5 hours.

5 5.65 g catalyst was obtained. Elemental analysis showed 0.098 wt% Zr and 13.17 wt% Al.

#### Example 16

##### Catalyst 16

10 A precursor solution was prepared by combining 5.0476 g of 30 wt% gel free methylaluminoxane in toluene (25.986 millimoles Al) and 0.0652 g of dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.104 millimoles Zr) with stirring. Then 2.1983 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace,  
15 Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 1.25. The solid had a consistency of damp sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.6 hours. 5.60 g finely divided, free-flowing solid catalyst was obtained. Elemental  
20 analysis showed 0.089 wt% Zr and 13.43 wt% Al.

#### Example 17

##### Catalyst 17

25 A precursor solution was prepared by combining 5.0552 g of 30 wt% gel free methylaluminoxane in toluene (26.025 millimoles Al) and 0.0654 g of dimethylsilylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride (0.104 millimoles Zr) with stirring. Then 7.8602 g of toluene was added. The precursor solution was added to 4.00 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.)  
30 previously heated to 600°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 2.25. The solid had the consistency of wet sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 50°C over 2.3 hours. 5.54 g finely divided, free-flowing solid catalyst was obtained. Elemental analysis showed 0.088 wt% Zr and 13.59 wt% Al.

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**Example 18****Catalyst 18**

A precursor solution was prepared by combining 13.3840 g of 30 wt% gel free methylaluminoxane in toluene (68.90 millimoles Al) and 0.1014 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (0.176 millimoles Zr) with stirring. Then 1.4120 g of toluene was added. The precursor solution was added to 9.4953 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.97. The finely divided, free-flowing solid was dried at reduced pressure (28 in. Hg vacuum) and a temperature as high as 40°C overnight. 13.183 g catalyst was obtained. Elemental analysis showed 0.09 wt% Zr and 13.25 wt% Al.

**Example 19****Catalyst 19**

A precursor solution was prepared by combining 4.2500 g of 30 wt% gel free methylaluminoxane in toluene (21.88 millimoles Al) and 0.0432 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (0.075 millimoles Zr) with stirring. Then 1.4120 g of toluene was added. The precursor solution was added to 4.005 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.97. The finely divided, free-flowing solid was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 2.5 hours. 5.185 g catalyst was obtained. Elemental analysis showed 0.10 wt% Zr and 10.64 wt% Al.

**Example 20****Catalyst 20**

A precursor solution was prepared by combining 3.5902 g of 30 wt% gel free methylaluminoxane in toluene (18.48 millimoles Al) and 0.0262 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (0.045 millimoles Zr) with stirring. Then 1.8979 g of toluene was added. The precursor solution was added to 4.0055 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.)



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previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.94. The finely divided, free-flowing solid was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 2.5 hours. 4.901 g catalyst was obtained. Elemental analysis showed 0.06 wt% Zr and 8.22 wt% Al.

#### Example 21

##### Catalyst 21

A precursor solution was prepared by combining 1.7072 g of 30 wt% gel free methylaluminoxane in toluene (8.79 millimoles Al) and 0.0257 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (0.045 millimoles Zr) with stirring. Then 3.5518 g of toluene was added. The precursor solution was added to 3.9309 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 0.94. The finely divided, free-flowing solid was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 3.2 hours. 4.400 g catalyst was obtained. Elemental analysis showed 0.07 wt% Zr and 4.76 wt% Al.

#### Example 22

##### Catalyst 22

A precursor solution was prepared by combining 106 g of 30 wt% gel free methylaluminoxane in toluene (546 millimoles Al) and 1.10 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (1.90 millimoles Zr) with stirring. Then 40 g of toluene was added. The precursor solution was added to 100 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 1.0. The solid which was not totally free flowing was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 3.25 hours. A finely divided, free-flowing solid catalyst was obtained. Elemental analysis showed 0.11 wt% Zr and 8.96 wt% Al.

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**Example 23****Catalyst 23**

A precursor solution was prepared by combining 108 g of 30 wt% gel free methylaluminoxane in toluene (554 millimoles Al) and 1.10 g of dimethylsilylbis(2-methyl-4,5-benzoinde-  
5 nyl)zirconium dichloride (1.90 millimoles Zr) with stirring. Then 72 g of toluene was added. The precursor solution was added to 100 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 1.25. The  
10 solid had a consistency of damp sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 3.25 hours. A finely divided, free-flowing solid catalyst was obtained. Elemental analysis showed 0.12 wt% Zr and 9.26 wt% Al.

**Example 24****Catalyst 24**

A precursor solution was prepared by combining 1.7940 g of 30 wt% gel free methylaluminoxane in toluene (9.236 millimoles Al) and 0.0135 g of dimethylsilylbis(2-methyl-4,5-benzoinde-  
20 nyl)zirconium dichloride (0.023 millimoles Zr) with stirring. Then 5.3578 g of toluene was added. The precursor solution was added to 2.0153 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica  
25 pore volume was 2.5. The solid had the consistency of wet sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 3 hours. 2.6172 g catalyst finely divided, free-flowing solid was obtained. Elemental analysis showed 0.11 wt% Zr and 8.82 wt% Al.

**Example 25****Catalyst 25**

A precursor solution was prepared by combining 0.8765 g of 30 wt% gel free methylaluminoxane in toluene (4.508 millimoles Al) and 0.0146 g of dimethylsilylbis(2-methyl-4,5-benzoinde-  
35 nyl)zirconium dichloride (0.025 millimoles Zr) with stirring. Then 6.2009 g of toluene was added. The precursor solution was added to 2.0015 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.)

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previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 2.5. The solid had the consistency of wet sand and was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 3 hours. 2.4446 g catalyst finely divided, free-flowing solid was obtained. Elemental analysis showed 0.09 wt% Zr and 5.11 wt% Al.

#### Comparative Example 26

#### Comparative Catalyst 26

A precursor solution was prepared by combining 6.8627 g of 30 wt% gel free methylaluminoxane in toluene (35.33 millimoles Al) and 0.0277 g of dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride (0.048 millimoles Zr) with stirring. Then 12.3745 g of toluene was added. The precursor solution was added to 2.0021 g of silica MS948, 1.6 cc/g P.V., available from W.R. Grace, Davison Chemical Division, Baltimore, Maryland (Davison Chemical Co.) previously heated to 800°C under N<sub>2</sub>. The ratio of liquid volume to total silica pore volume was 6.7 and produced a slurry which was dried at reduced pressure (29+ in. Hg vacuum) and a temperature as high as 60°C over 4.1 hours. 4.1414 g catalyst finely divided, free-flowing solid was obtained. Elemental analysis showed 0.09 wt% Zr and 18.82 wt% Al.

#### POLYMERIZATION TESTS FOR CATALYSTS 12 through 17

A sample of each of the supported catalyst (75 mg) made in the above Examples 12-17 was slurried in 2 ml of hexane and flushed with 250 mls of propylene into a 2 liter autoclave reactor, previously flushed with nitrogen, and containing triethylaluminum (0.5 ml of a 1 M solution in hexane) and 1000 ml of propylene at a temperature of 70°C. The reaction was run for 1 hour, at which time, the reactor was cooled, vented, and purged with nitrogen for 20 minutes. After the nitrogen purge, the reactor was opened, and the product was collected and dried in vacuo for a minimum of 2 hours at 75°C.

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**TABLE 2**

Catalyst	Metals* Loading		Mole Ratio Al/Zr	Percentage Pore Volume	g Polymer/ g Catalyst	g Polymer/ mg Zr	Percent Fouling **
	Al	Zr					
12	4.50	0.026	175	95	2387	3410	0.2
13	"	"	"	125	2253	3219	0
14	"	"	"	225	893	893	small chunks
15	6.50	"	250	95	2813	2870	2.0
16	"	"	"	125	2613	2936	0.2
17	"	"	"	225	2097	2383	small chunks

\* millimoles per gram silica

\*\* grams fouled polymer per total polymer obtained times 100%

5

**POLYMERIZATION TESTS FOR CATALYSTS 18 through C-26**

A sample of each of the supported catalyst made in the above Examples 18-  
C26 was slurried in 2 ml of hexane and flushed with 250 mls of propylene into a 2  
liter autoclave reactor, previously flushed with nitrogen, and containing  
10 triethylaluminum (0.5 ml of a 1 M solution in hexane) and 1000 ml of propylene,  
then the reactor is heated to a temperature of 65°C. The reaction was run for 1  
hour, at which time, the reactor was cooled, vented, and purged with nitrogen for  
20 minutes. After the nitrogen purge, the reactor was opened, and the product  
was collected and dried in vacuo for a minimum of 2 hours at 75°C. If there was  
15 any residual product (fouling) on the agitator or thermocouple, it was collected  
and weighed separately.

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**TABLE 3**

Catalyst	Metals* Loading		Mole Ratio Al/Zr	Percentage Pore Volume	g Polymer/ g Catalyst	g Polymer/ mg Zr	Percent Fouling **
	Al	Zr					
18	7.26	0.018	392	95	1571	1746	~5
19	5.46	0.019	293	97	2505	2087	0.5
20	4.61	0.011	407	94	1000	1099	0.5
21	2.24	0.011	197	94	595	495	0
22	5.50	0.019	286	100	1841	1674	0.1
23	5.50	0.019	291	125	796	796	0.1
24	4.58	0.012	395	250	562	562	0
25	2.25	0.013	178	250	425	472	0.1
C-26	17.65	0.024	737	670	2068	2783	100

\* millimoles per gram silica

\*\* grams fouled polymer per total polymer obtained times 100%

5

While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For example, it is within the scope of this invention to mix at least two of the catalysts of the invention or to use the catalyst of the invention with any other catalyst or catalyst system known in the art, for example a traditional Ziegler-Natta catalyst or catalyst system. Also the catalyst system of the invention can be used in a single reactor or in a series reactor. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

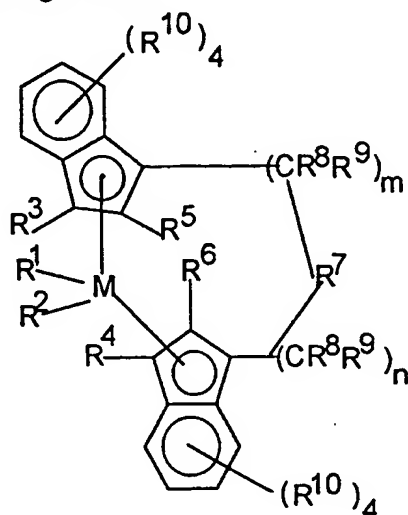
15

CLAIMS

We Claim:

1. A method for producing a supported catalyst system, said catalyst system  
 5 comprising a metallocene catalyst component, an alumoxane and a porous carrier,  
 said method comprising the steps of:

a) mixing said metallocene catalyst component and said alumoxane in  
 a solvent to form a solution wherein the metallocene catalyst component is  
 represented by the following formula:



10

wherein  $M^1$  is a metal of group 4, 5, or 6 of the Periodic Table,

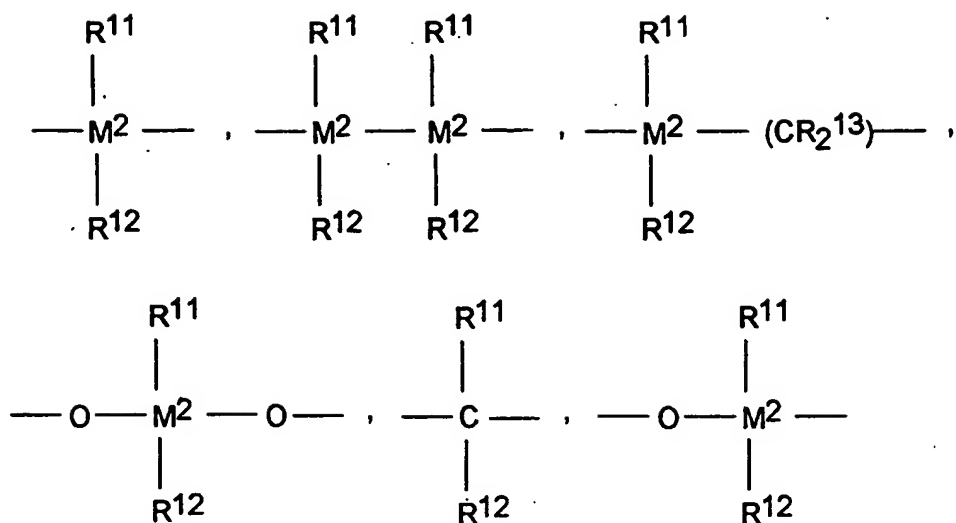
$R^1$  and  $R^2$  are identical or different, are one of a hydrogen atom, a  $C_1$ - $C_{10}$   
 alkyl group, a  $C_1$ - $C_{10}$  alkoxy group, a  $C_6$ - $C_{10}$  aryl group, a  $C_6$ - $C_{10}$  aryloxy  
 group, a  $C_2$ - $C_{10}$  alkenyl group, a  $C_7$ - $C_{40}$  arylalkyl group, a  $C_7$ - $C_{40}$  alkylaryl  
 15 group, a  $C_8$ - $C_{40}$  arylalkenyl group, or a halogen atom;

$R^3$  and  $R^4$  are hydrogen atoms;

$R^5$  and  $R^6$  are identical or different, preferably identical, are one of a  
 halogen atom, a  $C_1$ - $C_{10}$  alkyl group, which may be halogenated, a  $C_6$ - $C_{10}$  aryl  
 group, which may be halogenated, a  $C_2$ - $C_{10}$  alkenyl group, a  $C_7$ - $C_{40}$  arylalkyl  
 20 group, a  $C_7$ - $C_{40}$  alkylaryl group, a  $C_8$ - $C_{40}$  arylalkenyl group, a  $-NR_2^{15}$ ,  $-SR^{15}$ ,  
 $-OR^{15}$ ,  $-OSiR_3^{15}$  or  $-PR_2^{15}$  radical, wherein  $R^{15}$  is one of a halogen atom, a  $C_1$ -  
 $C_{10}$  alkyl group, or a  $C_6$ - $C_{10}$  aryl group;

$R^7$  is

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=BR<sup>11</sup>, =AIR<sup>11</sup>, -Ge-, -Sn-, -O-, -S-, =SO, =SO<sub>2</sub>, =NR<sup>11</sup>, =CO, PR<sup>11</sup>, or =P(O)R<sup>11</sup>;

5 wherein:

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> alkyl group, a C<sub>1</sub>-C<sub>20</sub> fluoroalkyl group, a C<sub>6</sub>-C<sub>30</sub> aryl group, a C<sub>6</sub>-C<sub>30</sub> fluoroaryl group, a C<sub>1</sub>-C<sub>20</sub> alkoxy group, a C<sub>2</sub>-C<sub>20</sub> alkenyl group, a C<sub>7</sub>-C<sub>40</sub> arylalkyl group, a C<sub>8</sub>-C<sub>40</sub> arylalkenyl group, C<sub>7</sub>-C<sub>40</sub> alkylaryl group, or R<sup>11</sup> and R<sup>12</sup>, or R<sup>11</sup> and R<sup>13</sup>, together with the atoms binding them, can form ring systems;

M<sup>2</sup> is silicon, germanium or tin;

R<sup>8</sup> and R<sup>9</sup> are identical or different and have the meanings as stated for R<sup>11</sup>;

15 m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2; and

the radicals R<sup>10</sup> are identical or different and have the meanings stated for R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> wherein further two adjacent R<sup>10</sup> radicals can be joined together to form a ring system; and

20

b) combining the solution and the porous carrier, wherein the total volume of the solution is less than that at which a slurry is formed.

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2. The method of claim 1 wherein the total volume of the solution is in the range of from less than three times the total pore volume of the porous support to above 1 times the total pore volume of the porous support.
- 5 3. The method of claim 1 or 2 wherein the total volume of the solution is in the range of from less than two times the total pore volume of the porous support to above one times the total pore volume of the porous support.
- 10 4. The method according to any of the preceding claims wherein the metallocene catalyst component comprises two or more metallocene catalyst components and/or wherein the mole ratio of aluminum of the alumoxane to the transition metal of the metallocene catalyst component is in the range of between 20:1 to less than 500:1.
- 15 5. The method according to any of the preceding claims wherein the method further comprises the step of prepolymerizing the supported catalyst system with an olefinic monomer.
- 20 6. The method according to any of the preceding claims wherein  $m=n=0$ ,  $M^2=\text{silicon}$ ,  $R^5 = R^6 = C_{1-10}$  alkyl, three of the  $R^{10}$  radicals = hydrogen and one is a  $C_{6-30}$  aryl group.
- 25 7. The method according to any of the preceding claims wherein the metallocene component is selected from the group consisting essentially of:  
rac-dimethylsilandiylbis(2-methyl-4,5-benzoindenyl) - zirconium dichloride;  
rac-dimethylsilandiylbis(2-methylindenyl)-zirconium dichloride;  
rac-dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)-zirconium  
dichloride;  
rac-dimethylsilandiylbis(2-methyl-4-phenylindenyl)zirconium dichloride;  
30 and  
rac-dimethylsilandiylbis(2-ethyl-4-phenylindenyl)zirconium dichloride.
- 35 8. A process for polymerizing propylene alone or in combination with one or more other olefins, said process comprising polymerizing in the presence of a supported catalyst system produced by the method of claim 1.
9. A supported catalyst system obtainable according to any of claims 1 - 7.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 95/07909

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 4/642

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0537686 (HOECHST AKTIENGESELLSCHAFT), 21 April 1993 (21.04.93), abstract, claims --	1-8
X	EP, A1, 0545303 (HOECHST AKTIENGESELLSCHAFT), 9 June 1993 (09.06.93), abstract, claims --	1-8
X	US, A, 5240894 (TERRY J. BURKHARDT ET AL), 31 August 1993 (31.08.93), abstract, example 1, claim 1 -----	1-8

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

26 Sept 1995

Date of mailing of the international search report

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Name and mailing address of the International Searching Authority



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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/08/95

International application No.

PCT/US 95/07909

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EP-A1- 0537686	21/04/93	AU-B- 659218	11/05/95
		AU-A- 2639592	22/04/93
		CA-A- 2080576	16/04/93
		JP-A- 5306304	19/11/93
		US-A- 5304614	19/04/94
		ZA-A- 9207905	21/04/93
EP-A1- 0545303	09/06/93	AU-B- 651914	04/08/94
		AU-A- 2972692	03/06/93
		CA-A- 2084015	31/05/93
		US-A- 5328969	12/07/94
		US-A- 5374752	20/12/94
		ZA-A- 9209214	26/05/93
US-A- 5240894	31/08/93	CA-A- 2135998	25/11/93
		EP-A- 0642536	15/03/95
		WO-A- 9323439	25/11/93